PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-054132

(43)Date of publication of application : 26.02.1999

(51)Int.Cl. H01M 6/16
H01M 10/40

(21)Application number : 09-209101

(22)Date of filing : 04.08.1997

(71)Applicant : SANYO ELECTRIC CO LTD

(72)Inventor : KUSUMOTO YASUYUKI
YOSHIMURA SEIJI
NOMA TOSHIYUKI
NISHIO KOJI

(54) NONAQUEOUS ELECTROLYTE BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To restrain self-discharge when a battery is preserved, and to improve a preserving characteristic by including dioxolane in an organic solvent containing isoxazole, oxazole, oxazoline and their derivatives.

SOLUTION: At least one kind selected from 3,5-dimethyl isoxazole, oxazole and 2-methyl-2-oxazoline is added as an additive to an organic solvent containing dioxolane ≥10 wt.%. When a nonaqueous electrolyte composed of this organic solvent and a solute is used, the additive reacts with lithium is the presence of dioxolane to form a good quality coating film on a negative electrode. Since this coating film restrains direct contact of lithium with the organic solvent, the decomposition of the nonaqueous electrolyte is restrained. An adding quantity of the additive is set to the range of about 0.01 to 30.0%, particularly desirably, 0.1 to 20.0% to the weight of the organic solvent. An electrode material to store/release lithium ions or metallic lithium can be exemplified as the negative electrode of a battery.

LEGAL STATUS

[Date of request for examination]	24.05.2001
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	3439083
[Date of registration]	13.06.2003
[Number of appeal against examiner's decision of	

rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

CLAIMS

[Claim(s)]
[Claim 1] A nonaqueous electolyte cell characterized by for said dioxolane containing 10% of the weight or more to said organic solvent, and containing at least one sort of additives chosen from a group which said organic solvent becomes from an isoxazole, oxazole, oxazoline, and those derivatives in a nonaqueous electolyte cell equipped with a nonaqueous electolyte which consists of a positive electrode, a negative electrode which consists of a possible negative-electrode material of occlusion bleedoff of a lithium or a lithium, an organic solvent containing dioxolane, and a solute.
[Claim 2] A nonaqueous electolyte cell according to claim 1 characterized by being at least one sort of additives chosen from a group which said additive becomes from 3, 5-dimethyl isoxazole, oxazole, and 2-methyl-2-oxazoline.
[Claim 3] A nonaqueous electolyte cell according to claim 2 by which said additive is characterized by being 3 and 5-dimethyl iso oxazoline.
[Claim 4] A nonaqueous electolyte cell according to claim 1 by which an addition of said additive is characterized by being 0.01 to 30.0% of the weight of a range to said organic solvent.
[Claim 5] A nonaqueous electolyte cell according to claim 4 by which an addition of said additive is characterized by being 0.1 to 20.0% of the weight of a range to said organic solvent.

[Translation done.]

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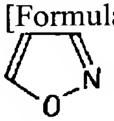
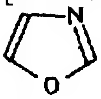
DETAILED DESCRIPTION

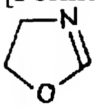
[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention relates to amelioration of the conservation property of the nonaqueous electrolyte cell which used the lithium as a negative-electrode active material, i.e., a lithium cell.
[0002]
[Description of the Prior Art] The lithium cell using a lithium as a negative-electrode active material attracts attention as a high energy density cell, and active research is done.
[0003] Generally by this seed cell, independence, such as ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, sulfolane, 1, 2-dimethoxyethane, tetrahydrofuran, 1, and 3-dioxolane, two components, or 3 component mixture is used as a solvent which constitutes a nonaqueous electolyte. And LiPF6, LiBF4, LiClO4, LiCF3SO3, LiASF6 and LiN (CF3SO2)2, and LiCF3(CF2)3SO3 grades can be enumerated as a solute dissolved into this.
[0004] By the way, raising the property of a cell is proposed by using for JP,60-91565,A the nonaqueous electrolyte which contains dioxolane in a solvent. However, if dioxolane is used for ** et al. and a solvent, in order to cause a reaction with the chemical negative electrode which uses a lithium as an active material, there is a problem that the cell capacity after conservation falls. Therefore, it has been an important technical problem in utilization of this seed cell to control the self-discharge at the time of conservation.
[0005] Then, although the method of adding a pyridine is in the electrolytic solution in order to raise a conservation property as indicated by JP,49-108525,A, also in this method, in the case of the cell using the organic solvent containing dioxolane, still sufficient property is not acquired but there is room of amelioration.
[0006]
[Problem(s) to be Solved by the Invention] This invention controls the self-discharge at the time of saving this seed cell, and proposes the outstanding nonaqueous electolyte which raises a conservation property.
[0007]
[Means for Solving the Problem] This invention is characterized by for said dioxolane containing 10% of the weight or more to said organic solvent, and containing at least one sort of additives chosen from a group which said organic solvent becomes from an isoxazole, oxazole, oxazoline, and those derivatives in a nonaqueous electolyte cell equipped with a nonaqueous electolyte which consists of a positive electrode, a negative electrode which consists of a possible negative-electrode material of occlusion bleedoff of a lithium or a lithium, an organic solvent containing dioxolane, and a solute.
[0008] It will be the basis of existence of dioxolane of the amount of specification, this additive will react with a lithium, and this reason will form a good coat on a negative electrode, if a nonaqueous electolyte which added one sort in an isoxazole as an additive, oxazole, oxazoline, or those derivatives is used for an organic solvent which contained dioxolane 10% of the weight or more. Since this coat controls direct contact to a lithium and an organic solvent, it is considered to control decomposition of a nonaqueous electolyte which makes contact to a lithium and the electrolytic solution **. Thus, it becomes possible to raise the conservation property of a cell.
[0009] Here, a structure expression of an isoxazole is shown in ** 1.
[0010]
[Formula 1]


[0011] The structure expression of oxazole is shown in ** 2.
[0012]

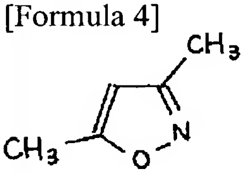
[Formula 2]



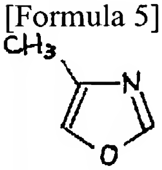
[0013] The structure expression of oxazoline is shown in ** 3.
[0014]
[Formula 3]



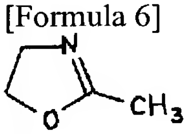
[0015] In the above-mentioned additive, -CH3 (methyl group), -C2H5 (ethyl group), or a halogen atom (fluorine F, chlorine Cl) replaces at least one hydrogen atom combined with the carbon atom of an isoxazole with the derivative of an isoxazole. Specifically, 3 and 5-dimethyl isoxazole shown in the following-ization 4 can be illustrated. The structure expression of 3 and 5-dimethyl isoxazole which is the derivative of an isoxazole is shown in ** 4.
[0016]
[Formula 4]



[0017] Moreover, -CH3 (methyl group), -C2H5 (ethyl group), or a halogen atom (fluorine F, chlorine Cl) replaces at least one hydrogen atom similarly combined with the carbon atom which constitutes each compound with the derivative of the derivative of oxazole. For example, 4-methyl oxazole as a derivative of oxazole shown in the following-ization 5 can be illustrated. The structure expression of 4-methyl oxazole is shown in ** 5.
[0018]
[Formula 5]



[0019] And -CH3 (methyl group), -C2H5 (ethyl group), or a halogen atom (fluorine F, chlorine Cl) replaces at least one hydrogen atom similarly combined with the carbon atom which constitutes each compound with the derivative of oxazoline. For example, the 2-methyl-2-oxazoline as a derivative of oxazoline shown in the following-ization 6 can be illustrated. The structure expression of 2-methyl-2-oxazoline is shown in ** 6.
[0020]
[Formula 6]



[0021] Also in said additive, or 3, 5-dimethyl isoxazole, oxazole, and 2-methyl-2-oxazoline tend to form the coat optimal on a negative electrode, they are considered to be easy to adsorb on a negative electrode, and they are desirable. The structure where this reason is expressed with ** 4, ** 2, and ** 6 tends to approach a lithium, and is presumed to be because for the electron distribution of each structure to have the gestalt which is easy to stick to a lithium metal, or it is because it has the structure of being easy to react. And also in this, control of the rate of self-discharge is much more attained in 3 and 5-dimethyl isoxazole.
[0022] And it is desirable to consider as 0.1 to 20.0% of the weight of a range preferably especially 30.0 or less % of the weight 0.01% of the weight or more to the weight of said organic solvent as an addition of said additive, and it is suitable from a viewpoint of controlling lowering of the discharge capacity after conservation of this seed nonaqueous electrolyte cell.
[0023] As a solute of this seed cell, although LiPF6, LiBF4, LiClO4, LiCF3SO3, LiASF6, LiN (CF3SO2)2 and LiN (C2F5SO2)2, LiCF3(CF2)3SO3, and LiC(CF3SO2)3 grade can be used, it is not limited to this.
[0024] as the organic solvent of this seed cell -- dioxolane -- it is possible independent or to use the mixture which contained dioxolane 10% of the weight or more, and added ethylene carbonate, propylene carbonate, butylene

carbonate, vinylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, the sulfolane, and the tetrahydrofuran here.

[0025] Although the metallic oxide containing manganese, cobalt, nickel, vanadium, and at least one sort of niobium can be used as a positive electrode of this seed cell, it is not limited to this.

[0026] As a negative electrode of this seed cell, what uses a lithium ion as occlusion and the matter which can be emitted, and uses a metal lithium as an electrode material electrochemically is illustrated. Considering a lithium ion as occlusion and matter which can be emitted, lithium alloys, such as carbon materials, such as a graphite, corks, and an organic substance baking object, and a lithium-aluminum alloy, a lithium-Magnesium alloy, a lithium-indium alloy, a lithium-tin alloy, a lithium-thallium alloy, a lithium-lead alloy, and a lithium-bismuth alloy, are illustrated electrochemically.

[0027]

[Embodiment of the Invention] Below, it explains in full detail per example of this invention.

(Experiment 1) Half section drawing of the flat form nonaqueous electolyte cell as one example of this invention is shown in drawing 1 . The negative electrode 1 which consists of a lithium metal is stuck to the inner surface of the negative-electrode charge collector 2 by pressure, and has fixed this negative-electrode charge collector 2 on the inner base of the negative-electrode can 3 of the shape of a cross section KO character which consists of ferritic stainless steel (SUS430). It is fixed to the interior of the insulating packing 4 made from polypropylene, the peripheral edge of the above-mentioned negative-electrode can 3 becomes the periphery of the insulating packing 4 from stainless steel, and the positive-electrode can 5 which makes the shape of a cross section KO character to an opposite direction is being fixed in the above-mentioned negative-electrode can 3. The positive-electrode charge collector 6 is being fixed to the inner base of this positive-electrode can 5, and the positive electrode 7 is being fixed to the inner surface of this positive-electrode charge collector 6. Between this positive electrode 7 and said negative electrode 1, the separator 8 with which impregnation of the nonaqueous electolyte which is the main point of this invention was carried out is infixed.

[0028] By the way, the manganese dioxide heat-treated at the temperature of 400 degrees C is used for said positive electrode 7 as an active material. Said heat treatment can be changed in a 350-430-degree C temperature requirement. This manganese dioxide, the carbon powder as an electric conduction agent, and the fluororesin powder as a binder are mixed by the weight ratio of 85:10:5, respectively. Next, after carrying out pressing of this mixture, desiccation processing was carried out at 300 degrees C, and the positive electrode 7 was produced. It can set up and this desiccation processing can be changed in a 250-350-degree C temperature requirement.

[0029] On the other hand, said negative electrode 1 is produced by piercing a lithium rolled plate in a predetermined size.

[0030] And 3 and 5-dimethyl isoxazole which is the derivative of the isoxazole as an additive is added at 1.0% of the weight of a rate to the weight of a mixed organic solvent to what dissolved the trifluoro methansulfonic acid lithium in the mixed organic solvent (they are five kinds, 10:0, 95:5, 9:1, 5:5, and 0:10, at a weight ratio) of propylene carbonate (PC) and dioxolane (DOXL) at a rate of one mol/l. as a solute as the electrolytic solution, and it is non-******. **** is obtained This nonaqueous electolyte is used and they are the cell A1 with an outer diameter [of 20.0mm], and a thickness of 2.5mm - A5. It produced.

(Experiment 2) It replaced with 3 and 5-dimethyl isoxazole used in said experiment 1, and a cell B1 - B5 were similarly produced except having used oxazole as an additive.

(Experiment 3) having replaced with 3 and 5-dimethyl isoxazole used in said experiment 1, and having used the 2-methyl-2-oxazoline which is the derivative of oxazoline as an additive -- with -- Outside produced cells C1-C5 similarly.

(Experiment 4) The same cell was produced using the electrolytic solution which does not add 3 and 5-dimethyl isoxazole in said experiment 1, and this was made into cells X1-X5.

[0031] The conservation property of each cell was compared using these cells A1 - A5, B1 - B5, C1-C5, and X1-X5. After this experiment condition produced each cell and saved it for two months at 60 degrees C, it made the cell discharge actually and the rate of self-discharge (%) was provided by it as a percentage to the capacity before saving that difference as compared with the capacity before conservation. This result is shown in a table 1.

[0032]

[A table 1]

溶媒混合重量比 PC：DOXL		10：0	95：5	9：1	5：5	0：10
添加剤	3,5-ジメチルイソオキサゾール	A1 9.0	A2 8.0	A3 4.0	A4 3.1	A5 2.7
	オキサゾール	B1 9.0	B2 8.0	B3 4.2	B4 3.2	B5 2.9
	2-メチル-2-オキサゾリン	C1 9.0	C2 8.0	C3 4.4	C4 3.4	C5 3.1
なし		X1 9.0	X2 9.5	X3 10.0	X4 11.0	X5 12.0

[0033] As for this invention cell A3 - A5, B3 - B5, and C3-C5, this table 1 shows that the rate of self-discharge is small, lowering of the cell capacity at the time of conservation is suppressed, and self-discharge is controlled as compared with the comparison cells A1, A2, and B1, B-2, C1 and C2, and X1-X5.
(Experiment 5) Cell A4 of said experiment 1, cell B4 and the cell C4, and the cell that has the same configuration were produced, the addition of 3 added to a nonaqueous electolyte, 5-dimethyl isoxazole, oxazole, and 2-methyl-2-oxazoline was changed, and the discharge capacity of the cell after conservation was measured. This experiment condition was saved for two months at 60 degrees C after producing each cell, and surveyed discharge capacity (mAh) of a cell.
[0034] This result is shown in a table 2. A table 2 shows the addition of 3 to nonaqueous electolyte weight, 5-dimethyl isoxazole, oxazole, and 2-methyl-2-oxazoline, and the relation of the rate of self-discharge (%). In addition, calculation of this rate of self-discharge is the same as said experiment 1.
[0035]
[A table 2]

添加量 (重量%)	自己放電率 (%)		
	3,5-ジメチルイソオキサゾール	オキサゾール	2-メチル-2-オキサゾリン
0	11.0	11.0	11.0
0.01	7.5	7.4	7.5
0.1	6.0	6.0	6.0
1	3.1	3.2	3.4
5	2.7	2.6	4.0
10	3.9	3.8	4.6
20	5.9	6.0	6.1
30	7.4	7.5	7.6

[0036] As an addition of 3, 5-dimethyl isoxazole, oxazole, and 2-methyl-2-oxazoline, to the weight of an organic solvent, the addition effect was accepted in 0.01 to 30.0% of the weight of the range, and lowering of the cell capacity after conservation is controlled from this result. As this addition, it is especially desirable from a viewpoint that 20.0% of the weight of a range does not reduce the discharge capacity of the cell after conservation from 0.1 % of the weight of additions.
[0037] In addition, although the addition of 3, 5-dimethyl isoxazole, oxazole, and 2-methyl-2-oxazoline is changed in the experiment 5, the same inclination is observed even if it is a cell using the derivative of other additives, i.e., said additive, an isoxazole, or oxazoline.
[0038] although trifluoro methansulfonic acid lithium LiCF3SO3 was shown in each above-mentioned example as a solute dissolved in a nonaqueous electolyte -- LiPF6, LiClO4, LiBF4, LiN (CF3SO2)2, LiN (C2F5SO2)2, LiC (CF3SO3)3, and LiCF3(CF2) 3 -- it cannot be overemphasized that SO3 and LiAsF6 can be used. Moreover, although the mixed solvent of propylene carbonate and dioxolane was illustrated as an organic solvent, it is possible to use the mixture which contained dioxolane 10% of the weight or more, and added butylene carbonate, vinylene carbonate,

dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, and a tetrahydrofuran here.
[0039]
[Effect of the Invention] As mentioned above, the conservation property of this seed cell can be raised by adding at least one sort in the isoxazole which is an additive, oxazole, oxazoline, and these derivatives to a nonaqueous electolyte. And especially as said additive, one sort in 3, 5-dimethyl isoxazole, oxazole, and 2-methyl-2-oxazoline is suitable, and especially 3 and 5-dimethyl isoxazole is suitable also in this. Furthermore, speaking of the addition of an additive, 0.01 to 30.0% of the weight of a range is suitable to the weight of said organic solvent, 0.1 to 20.0% of the weight of a range, then the conservation property of a cell can be improved especially notably, and the industrial value is very large.

[Translation done.]